

AMENDMENT

(Amendment under the provision of Article 11 of the Law [according to PCT Article 34(2)(b)])

To: Commissioner of the Patent Office

1. Identification of the International Application

PCT/JP03/007460

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4. Items to be Amended

Description and Claim

5. Content of Amendment

(1) Page 7, line 20 (page 11, line 5 of English translation version), change "(Examples 1 to 23)" to  
-- Examples 1 to 22 --.

- (2) Page 9, Table 1, (page 12, Table 1 of English translation version) of Example 15, change “ $\text{Cu}_{42.5}\text{Zr}_{42.5}\text{Ga}_5$ ” to --  $\text{Cu}_{52.5}\text{Zr}_{42.5}\text{Ga}_5$ --.
- (3) Page 9, Table 1, (page 12, Table 1 of English translation version), delete “Example 18”.
- (4) Page 9, Table 1, (page 12, Table 1 of English translation version), change “Example 19” to -- Example 18 --.
- (5) Page 9, Table 1, (page 12, Table 1 of English translation version), change “Example 20” to -- Example 19 --.
- (6) Page 9, Table 1, (page 12, Table 1 of English translation version), change “Example 21” to -- Example 20 --.
- (7) Page 9, Table 1, (page 12, Table 1 of English translation version), change “Example 22” to -- Example 21 --.
- (8) Page 9, Table 1, (page 12, Table 1 of English translation version), change “Example 23” to -- Example 22 --.
- (9) Page 10, Table 2, (page 13, Table 2 of English translation version) of Example 15, change “ $\text{Cu}_{42.5}\text{Zr}_{42.5}\text{Ga}_5$ ” to --  $\text{Cu}_{52.5}\text{Zr}_{42.5}\text{Ga}_5$ --.
- (10) Page 10, Table 2, (page 13, Table 2 of English translation version), delete “Example 18”.
- (11) Page 10, Table 2, (page 13, Table 2 of English translation version), change “Example 19” to -- Example 18 --.
- (12) Page 10, Table 2, (page 13, Table 2 of English translation version), change “Example 20” to -- Example 19 --.
- (13) Page 10, Table 2, (page 13, Table 2 of English translation version), change “Example 21” to -- Example 20 --.

- (14) Page 10, Table 2, (page 13, Table 2 of English translation version), change "Example 22" to -- Example 21 --.
- (15) Page 10, Table 2, (page 13, Table 2 of English translation version), change "Example 23" to -- Example 22 --.
- (16) Page 11, line 20, (page 15, line 18 of English translation version), change "891 at maximum" to -- 698 at maximum --.
- (17) Claim 1, change "atomic percent and 2 atomic percent  $\leq b \leq 10$  atomic percent]" to -- atomic percent, 2 atomic percent  $\leq b \leq 10$  atomic percent, and Cu being 50 atomic percent or more --.
- (18) Claim 1, change "where  $T_x$  represents a crystallization initiation temperature and" to -- where  $T_x$  represents a crystallization initiation temperature,  $T_x$  being 770K or more and --.
- (19) Claim 2, change "and  $b + c + d + e \leq 15$  atomic percent]" to --  $b + c + d + e \leq 15$  atomic percent, and Cu being 50 atomic percent or more] --.
- (20) Claim 2, change "where  $T_x$  represents a crystallization initiation temperature and" to -- where  $T_x$  represents a crystallization initiation temperature,  $T_x$  being 770K or more and -- .

6. Attachments (1) pages 7, 9 to 11 (pages 11 to 15 of English translation version) of specification  
page 13 (pages 17 to 18 of English translation version) of claims

## (Examples)

The examples of the present invention will be described below. Mother alloys were prepared through melting from materials having alloy compositions shown in Table 1 (Examples 5 1 to 22) by an arc melting method. Thereafter, thin ribbon samples of about 20  $\mu\text{m}$  were prepared by a single-roll liquid quenching process. Subsequently, the glass transition temperature ( $T_g$ ) and the crystallization initiation temperature ( $T_x$ ) of the thin ribbon sample were measured with 10 a differential scanning calorimeter (DSC). The supercooled liquid region ( $T_x - T_g$ ) was calculated from these values. The liquid phase line temperature ( $T_l$ ) was measured by a differential thermal analysis (DTA). The reduced glass transition temperature ( $T_g/T_l$ ) was calculated from these 15 values. A rod-shaped sample having a diameter of 1 mm was prepared by the mold casting method, and an amorphous state of the sample was checked by an X-ray diffraction method.

The volume fraction ( $V_f\text{-amo.}$ ) of amorphous phase contained in the sample was evaluated by using DSC based on 20 the comparison of calorific value of the sample during crystallization with that of a completely amorphous thin ribbon having a thickness of about 20  $\mu\text{m}$ . These evaluation results are shown in Table 1. Furthermore, a compression test piece was prepared. A compression test was performed with an 25 Instron type testing machine, and the compressive strength ( $\sigma_f$ ) and the Young's modulus ( $E$ ) were evaluated. The Vickers hardness ( $H_v$ ) was measured. The measurement results are shown

in Table 2.

Fig. 1 shows DSC curves of amorphous bulk materials of Cu-Zr-Al alloys. Fig. 2 shows X-ray diffraction patterns. Fig. 3 shows stress-strain curves based on the compression test of the amorphous bulk materials of the Cu-Zr-Al alloys.

(Table 1)

	Alloy composition (at%)	T <sub>g</sub> (K)	T <sub>x</sub> (K)	T <sub>x-T<sub>g</sub></sub> (K)	T <sub>g</sub> /T <sub>m</sub>	V <sub>f</sub> -Amo.
Example 1	Cu <sub>60</sub> Zr <sub>35</sub> Al <sub>5</sub>	755	801	46	0.59	100
Example 2	Cu <sub>55</sub> Zr <sub>40</sub> Al <sub>5</sub>	723	800	77	0.62	100
Example 3	Cu <sub>50</sub> Zr <sub>45</sub> Al <sub>5</sub>	701	770	69	0.60	100
Example 4	Cu <sub>52.5</sub> Zr <sub>42.5</sub> Al <sub>5</sub>	709	781	72	0.61	100
Example 5	Cu <sub>55</sub> Zr <sub>42.5</sub> Al <sub>2.5</sub>	705	773	68	0.61	100
Example 6	Cu <sub>55</sub> Hf <sub>40</sub> Al <sub>5</sub>	777	862	85	0.60	100
Example 7	Cu <sub>50</sub> Hf <sub>45</sub> Al <sub>5</sub>	765	857	92	0.62	100
Example 8	Cu <sub>52.5</sub> Hf <sub>40</sub> Al <sub>7.5</sub>	779	834	55	0.63	100
Example 9	Cu <sub>50</sub> Hf <sub>42.5</sub> Al <sub>7.5</sub>	780	835	55	0.63	100
Example 10	Cu <sub>52.5</sub> Hf <sub>42.5</sub> Al <sub>5</sub>	771	849	78	0.59	100
Example 11	Cu <sub>55</sub> Hf <sub>37.5</sub> Al <sub>7.5</sub>	776	863	87	0.61	100
Example 12	Cu <sub>55</sub> Hf <sub>42.5</sub> Al <sub>2.5</sub>	769	831	62	0.60	100
Example 13	Cu <sub>50</sub> Zr <sub>22.5</sub> Hf <sub>22.5</sub> Al <sub>5</sub>	790	843	53	0.62	100
Example 14	Cu <sub>55</sub> Zr <sub>40</sub> Ga <sub>5</sub>	730	780	50	0.61	100
Example 15	Cu <sub>52.5</sub> Zr <sub>42.5</sub> Ga <sub>5</sub>	728	777	49	0.61	100
Example 16	Cu <sub>55</sub> Hf <sub>40</sub> Ga <sub>5</sub>	784	847	63	0.58	100
Example 17	Cu <sub>50</sub> Zr <sub>45</sub> Al <sub>2.5</sub> Ga <sub>2.5</sub>	728	792	64	0.61	100
Example 18	Cu <sub>50</sub> Zr <sub>40</sub> Al <sub>5</sub> Nb <sub>5</sub>	721	771	50	0.61	100
Example 19	Cu <sub>50</sub> Zr <sub>40</sub> Al <sub>5</sub> Au <sub>5</sub>	735	815	80	0.61	100
Example 20	Cu <sub>50</sub> Zr <sub>40</sub> Al <sub>5</sub> Y <sub>5</sub>	721	795	74	0.61	100
Example 21	Cu <sub>50</sub> Zr <sub>45</sub> Al <sub>2.5</sub> Sn <sub>2.5</sub>	707	785	78	0.61	100
Example 22	Cu <sub>50</sub> Zr <sub>45</sub> Al <sub>2.5</sub> B <sub>2.5</sub>	713	792	79	0.61	100
Comparative example 1	Cu <sub>70</sub> Zr <sub>20</sub> Al <sub>10</sub>	-	-	-	-	50<

Comparative example 2	Cu <sub>70</sub> Hf <sub>20</sub> Al <sub>10</sub>	-	-	-	-	50<
Comparative example 3	Cu <sub>55</sub> Zr <sub>20</sub> Al <sub>5</sub> Ni <sub>10</sub>	-	-	-	-	50<
Comparative example 4	Cu <sub>60</sub> Al <sub>40</sub>	-	-	-	-	10<
Comparative example 5	Cu <sub>60</sub> Zr <sub>30</sub> Ti <sub>10</sub>	713	750	37	0.61	100
Comparative example 6	Cu <sub>60</sub> Hf <sub>20</sub> Ti <sub>20</sub>	730	768	38	0.61	100
Comparative example 7	Cu <sub>60</sub> Zr <sub>40</sub>	717	777	60	0.60	91
Comparative example 8	Cu <sub>55</sub> Zr <sub>35</sub> Ti <sub>10</sub>	680	727	47	0.59	100
Comparative example 9	Cu <sub>53</sub> Zr <sub>35</sub> Al <sub>5</sub> Ti <sub>7</sub>	721	753	32	0.54	50<

(Table 2)

	Alloy composition (at%)	$\sigma_f$ (MPa)	E (GPa)	Hv
Example 1	Cu <sub>60</sub> Zr <sub>35</sub> Al <sub>5</sub>	2265	119	603
Example 2	Cu <sub>55</sub> Zr <sub>40</sub> Al <sub>5</sub>	2220	116	581
Example 3	Cu <sub>50</sub> Zr <sub>45</sub> Al <sub>5</sub>	1921	103	546
Example 4	Cu <sub>52.5</sub> Zr <sub>42.5</sub> Al <sub>5</sub>	2130	112	568
Example 5	Cu <sub>55</sub> Zr <sub>42.5</sub> Al <sub>2.5</sub>	2200	115	589
Example 6	Cu <sub>55</sub> Hf <sub>40</sub> Al <sub>5</sub>	2280	121	642
Example 7	Cu <sub>50</sub> Hf <sub>45</sub> Al <sub>5</sub>	2320	134	667
Example 8	Cu <sub>52.5</sub> Hf <sub>40</sub> Al <sub>7.5</sub>	2295	128	644
Example 9	Cu <sub>50</sub> Hf <sub>42.5</sub> Al <sub>7.5</sub>	2372	137	673
Example 10	Cu <sub>52.5</sub> Hf <sub>42.5</sub> Al <sub>5</sub>	2380	137	681
Example 11	Cu <sub>55</sub> Hf <sub>37.5</sub> Al <sub>7.5</sub>	2412	140	698
Example 12	Cu <sub>55</sub> Hf <sub>42.5</sub> Al <sub>2.5</sub>	2253	131	692
Example 13	Cu <sub>50</sub> Zr <sub>22.5</sub> Hf <sub>22.5</sub> Al <sub>5</sub>	2130	122	591
Example 14	Cu <sub>55</sub> Zr <sub>40</sub> Ga <sub>5</sub>	2219	117	585
Example 15	Cu <sub>52.5</sub> Zr <sub>42.5</sub> Ga <sub>5</sub>	2100	115	571
Example 16	Cu <sub>55</sub> Hf <sub>40</sub> Ga <sub>5</sub>	2275	126	652
Example 17	Cu <sub>50</sub> Zr <sub>45</sub> Al <sub>2.5</sub> Ga <sub>2.5</sub>	2205	115	691
Example 18	Cu <sub>50</sub> Zr <sub>40</sub> Al <sub>5</sub> Nb <sub>5</sub>	2312	131	674
Example 19	Cu <sub>50</sub> Zr <sub>40</sub> Al <sub>5</sub> Au <sub>5</sub>	2245	117	597
Example 20	Cu <sub>50</sub> Zr <sub>40</sub> Al <sub>5</sub> Y <sub>5</sub>	2180	114	575
Example 21	Cu <sub>50</sub> Zr <sub>45</sub> Al <sub>2.5</sub> Sn <sub>2.5</sub>	2200	112	561
Example 22	Cu <sub>50</sub> Zr <sub>45</sub> Al <sub>2.5</sub> B <sub>2.5</sub>	2175	119	559
Comparative example 1	Cu <sub>70</sub> Zr <sub>20</sub> Al <sub>10</sub>	-	-	564

Comparative example 2	Cu <sub>70</sub> Hf <sub>20</sub> Al <sub>10</sub>	-	-	624
Comparative example 3	Cu <sub>55</sub> Zr <sub>30</sub> Al <sub>5</sub> Ni <sub>10</sub>	-	-	578
Comparative example 4	Cu <sub>60</sub> Ti <sub>40</sub>	-	-	566
Comparative example 5	Cu <sub>60</sub> Zr <sub>30</sub> Ti <sub>10</sub>	2115	114	504
Comparative example 6	Cu <sub>60</sub> Hf <sub>20</sub> Ti <sub>20</sub>	2080	135	620
Comparative example 7	Cu <sub>60</sub> Zr <sub>40</sub>	1880	102	555
Comparative example 8	Cu <sub>55</sub> Zr <sub>35</sub> Ti <sub>10</sub>	1860	112	567
Comparative example 9	Cu <sub>35</sub> Zr <sub>35</sub> Al <sub>5</sub> Ti <sub>7</sub>	-	-	584

As is clear from Table 1, with respect to the amorphous alloy of each Example, the Cu-Hf or Cu-Zr-Hf amorphous alloy exhibits  $\Delta T_x$  of a large 50 K or more, even the Cu-Zr amorphous alloy exhibits  $\Delta T_x$  of 45 K or more, the reduced glass transition temperature of 0.57 or more is exhibited, and an amorphous alloy rod having a diameter of 1 mm was readily produced.

On the other hand, in the alloys of Comparative examples 1 and 2, (Al,Ga) is 10 atomic percent while (Zr,Hf) is less than 35 atomic percent, a high glass-forming ability is not exhibited, and no rod-shaped amorphous alloy having a diameter of 1 mm was produced.

In the alloy of Comparative example 3, the amount of Ni exceeds 5 atomic percent, a high glass-forming ability is not exhibited, and no rod-shaped amorphous alloy having a diameter of 1 mm was produced. In the alloy of Comparative example 4, no basic element (Zr,Hf) is present, nor was rod-shaped

amorphous alloy having a diameter of 1 mm produced. In the alloys of Comparative examples 5 and 6, no fundamental element (Al, Ga) is present. Although an rod-shaped amorphous alloy having a diameter of 1 mm was produced, the supercooled liquid 5 region is less than 45 K, and excellent workability is not exhibited.

In the alloys of Comparative examples 7 and 8, Zr is 35 atomic percent or more, the supercooled liquid region is 45 K or more, and excellent workability is exhibited. However, the 10 compressive strength is small.

In the alloy of Comparative example 9, when Ti exceeded 5 atomic percent, the reduced glass transition temperature Tg/Tl was significantly reduced and, therefore, no rod-shaped amorphous alloy having a diameter of 1 mm was produced.

As is clear from Table 2, the amorphous alloy of each Example exhibits the compressive fracture strength ( $\sigma_f$ : MPa) of 1,921 at minimum and 2,412 at maximum, the hardness (room temperature Vickers hardness: Hv) of 546 at minimum and 698 at maximum, and the Young's modulus (E: GPa) of 103 at minimum 20 and 140 at maximum, so that the compressive fracture strength of 1,900 MPa or more, the Vickers hardness of 500 Hv or more, and the Young's modulus of 100 GPa or more are exhibited.

#### Industrial Applicability

As described above, according to the Cu-based alloy compositions of the present invention, rod-shaped samples of 1 mm or more can be readily prepared by the mold casting method.

## CLAIMS

1. A Cu-based amorphous alloy comprising 90 percent by volume or more of amorphous phase having a composition represented by  
5 Formula:  $Cu_{100-a-b}(Zr,Hf)_a(Al,Ga)_b$  [in Formula, a and b are on an atomic percent basis and satisfy  $35 \text{ atomic percent} \leq a \leq 50$  atomic percent,  $2 \text{ atomic percent} \leq b \leq 10 \text{ atomic percent}$ , and Cu being 50 atomic percent or more, wherein the temperature interval  $\Delta T_x$  of supercooled liquid region is 45 K or more, the  
10 temperature interval being represented by Formula  $\Delta T_x = T_x - T_g$  (where  $T_x$  represents a crystallization initiation temperature,  $T_x$  being 770K or more and  $T_g$  represents a glass transition temperature.), a rod or a sheet having a diameter or thickness of 1 mm or more and a volume fraction of  
15 amorphous phase of 90% or more can be produced by a metal mold casting method, the compressive strength is 1,900 MPa or more, the Young's modulus is 100 GPa or more, and the Vickers hardness is 500 Hv or more.
2. A Cu-based amorphous alloy comprising 90 percent by volume or more of amorphous phase having a composition represented by  
20 Formula:  $Cu_{100-a-b}(Zr,Hf)_a(Al,Ga)_bM_cT_dQ_e$  [in Formula, M represents at least one element selected from the group consisting of Fe, Ni, Co, Ti, Cr, V, Nb, Mo, Ta, W, Be, and rare-earth elements, T represents at least one element selected from the group  
25 consisting of Ge, Sn, Si, and B, Q represents at least one element selected from the group consisting of Ag, Pd, Pt, and Au, a, b, c, d, and e are on an atomic percent basis and

satisfy  $35 \text{ atomic percent} \leq a \leq 50 \text{ atomic percent}$ ,  $2 \text{ atomic percent} \leq b \leq 10 \text{ atomic percent}$ ,  $0 \leq c \leq 5\%$ ,  $0 \leq d \leq 5\%$ ,  $0 \leq e \leq 5\%$ ,  $b + c + d + e \leq 15 \text{ atomic percent}$ , and Cu being 50 atomic percent or more], wherein the temperature interval  $\Delta T_x$  of supercooled liquid region is 45 K or more, the temperature interval being represented by Formula  $\Delta T_x = T_x - T_g$  (where  $T_x$  represents a crystallization initiation temperature,  $T_x$  being 770K or more and  $T_g$  represents a glass transition temperature.), a rod or a sheet having a diameter or thickness of 1 mm or more and a volume fraction of amorphous phase of 90% or more can be produced by a metal mold casting method, the compressive strength is 1,900 MPa or more, the Young's modulus is 100 GPa or more, and the Vickers hardness is 500 Hv or more.